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(11) Anmelder:
EMTEC Magnetics GmbH, 67059 Ludwigshafen, DE

(12) Erfinder:
Ilmer, Andreas, Dr., 67069 Ludwigshafen, DE; Lenz,
Werner, Dr., 67098 Bad Dürkheim, DE; Kress, Ria,
Dr., 67063 Ludwigshafen, DE; Heilmann, Peter, Dr.,
67098 Bad Dürkheim, DE; Veitch, Ronald, Dr., 67133
Maxdorf, DE; Jakusch, Helmut, Dr., 67227
Frankenthal, DE; Hoffmann, Erich, Dipl.-Ing., 69126
Heidelberg, DE

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(54) Magnetischer Aufzeichnungsträger mit hoher Aufzeichnungsdichte

(55) Neuerdings sind digitale Aufzeichnungsverfahren bekannt geworden, bei denen der Aufzeichnungsträger vor einer Aufzeichnung kein Löschfeld passiert. Derartige Aufzeichnungsträger müssen folglich ein gutes Überschreibverhalten aufweisen. Es wurde gefunden, daß diese Forderung erfüllt wird mit doppelschichtig aufgebauten Aufzeichnungsträgern, wobei die obere Schicht ein Metall- oder Metall-Legierungspulver enthält und eine Dicke von weniger als 0,3 µm besitzt und wobei die untere Schicht ein magnetisches Pigment enthält. Die Koerzitivkraft der unteren Schicht beträgt höchstens zwei Drittel der Koerzitivkraft der oberen Schicht und die remanente Magnetisierung der unteren Schicht beträgt mindestens 32 kA/m.

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Magnetic recording medium having a high recording density

The present invention relates to a magnetic recording medium which comprises at least two layers on a nonmagnetic substrate, the lower layer containing at least one pigment and one binder and the upper binder-containing layer containing a metal powder or metal alloy powder as magnetic pigment.

Modern magnetic recording media meet the constantly growing requirements only when they permit larger storage capacities, faster access time and higher transmission rates of the stored information. These recording media must therefore on the one hand have a structure such that the magnetic pigments in the recording layer have a sufficiently high density to ensure high storage capacities but, on the other hand, the thickness of the magnetic layer must be very small to permit direct overwriting of the data during re-recording without a prior erasing process. For example, magnetic recording media having high storage capacity today have magnetic layers which are only less than about 1 μm thick.

To realize such thin magnetic layers having high storage density, magnetic recording media in which a binder-free ferromagnetic metal layer having a very small thickness was applied by means of vacuum technology were developed in recent years. Although the recording media thus produced reach a high playback level, the mass production of such media still presents considerable difficulties in comparison with magnetic recording media in which the magnetic pigments are dispersed in binders. Since these ME tapes cannot be stored without change under the influence of atmospheric oxygen, their use too presents problems.

New developments in recent years have shown that the requirement for smaller layer thickness can also be met by a

thin magnetic layer in which the finely divided magnetic particles are dispersed in a polymeric binder matrix and which is applied to a nonmagnetic lower layer.

5 Such recording media are described, for example, in US
2 819 186, German Laid-Open Application DOS 4,302,516,
European Patents 0 520 155, 0 566 100, 0 566 378 and
0 682 802 and German Laid-Open Applications DOS 4,443,896,
195 04 930, 195 11 872, 195 11 873, 195 11 875 and
10 195 11 876.

The abovementioned magnetic recording media describe media which are composed of two layers and in which the upper magnetic layer has a thickness of from 0.01 to about 1 μm , preferably 0.1-0.4 μm . The thickness of the lower nonmagnetic layer is 0.5-8 μm . The upper layer preferably contains finely divided magnetic metal or metal alloy particles while the lower nonmagnetic layer contains finely divided nonmagnetic pigments which, in some cases, have an acicular structure, as described, for example, in the abovementioned publications European Patents 0 566 378 and 0 682 802.

25 Investigations by the Applicant have confirmed that the overwrite behavior of double-layer magnetic recording media is dependent primarily on the thickness of the magnetic upper layer. The desirable good overwrite behavior of metal evaporated tapes (referred to below as ME tapes) can be achieved, for example, by making the upper layer extremely thin (e.g. 0.12 μm).

30 However, it is observed that, in particular in recording at relatively long wavelengths, the output level too decreases with decreasing magnetic layer thickness, i.e. output level and overwritability exhibit opposite behavior. However, a low output level generally leads to a higher susceptibility

of the recorded signal to faults, which manifests itself in an increased bit error rate during digital recording.

However, the bit error rate is also increased by poor overwritability since, in this case, an old recording is only insufficiently erased and hence the quality of the new recording is impaired. If this effect is too great and errors can no longer be corrected, the recording can no longer be played back. Metal pigment tapes (referred to below as MP tapes) have a lower output level than ME tapes with the same thickness of the magnetic layer. Raising the output level by increasing the thickness of the magnetic layer would lead to poorer overwritability.

It is an object of the present invention to provide a binder-containing magnetic recording medium which simultaneously achieves good overwritability and a high playback level.

We have found that this object is surprisingly achieved, according to the invention, by a magnetic recording medium which comprises at least two layers on a nonmagnetic substrate, the lower layer containing at least one pigment and one binder and the upper binder-containing layer containing a metal powder or metal alloy powder as magnetic pigment and having a thickness of less than 0.3 µm, wherein the lower layer contains a magnetic pigment, so that the coercive force of the lower layer is not more than two thirds of the coercive force of the upper layer, and the residual induction of the lower layer is at least 32 kA/m.

In a preferred embodiment, the coercive force of the lower layer is not more than half the coercive force of the upper layer.

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Further details of the invention are evident from the following description, the drawings and the Examples.

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Figure 1 shows the change in the overwritability in dB as a function of the thickness of the magnetic upper layer, using an MP tape with a nonmagnetic lower layer as an example.

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Figure 2 shows the change in the output level in dB at a recording wavelength of 3 μm as a function of the thickness of the magnetic upper layer, using an MP tape with a nonmagnetic lower layer as an example.

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Figure 3 shows the overwrite ratios as a function of the frequency of the overwritten signal for magnetic recording media having virtually the same thickness of the upper layer for an Example according to the invention and for a Comparative Example.

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Figure 4 shows the overwrite ratios as a function of the output level at 3 μm wavelength of the signal to be overwritten for a magnetic and a nonmagnetic lower layer.

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Below, the novel magnetic recording medium is explained in more detail.

Suitable nonmagnetic flexible substrates are known films of polyesters, such as polyethylene terephthalate or polyethylene naphthalate, and polyolefins, cellulose triacetate, polycarbonates, polyamides, polyimides, polyamidoimides, polysulfones, aramids or aromatic polyamides.

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According to the invention, the lower layer contains magnetic pigments whose magnetic values are established so that they do not interfere with the recording on the upper magnetic layer.

Acicular magnetic chromium oxide pigments which have a specific surface area (determined by the BET method) of from 50 to 100 m²/g and a coercive force H_c of from 15 to 40, preferably 20-30, kA/m have proven particularly suitable.

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According to the invention, γ -Fe₂O₃ pigments, in particular cobalt-doped γ -Fe₂O₃, having a coercive force H_c of 15-80, preferably 50-70, kA/m and a specific surface area, determined by the BET method, of 30-50 m²/g, and magnetites, ferrites or metal powders can also be used as magnetic pigments in the lower layer.

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These pigments may be used either alone or as mixtures with one another or with further inorganic or organic, in particular nonmagnetic pigments.

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The residual induction Mr in the longitudinal direction of the magnetic recording medium is established by the saturation magnetization of the magnetic pigment and its amount and orientation. The residual induction of the lower magnetic layer here should be at least 32, preferably at least 35, in particular at least 40, kA/m.

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However, the residual induction of the lower layer should not be higher than 150 kA/m, in order to avoid impairment of the recording behavior of the upper layer by the lower layer.

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The mean particle length of the magnetic pigments of the lower layer is 0.05-0.25 μ m, preferably from 0.1 to 0.2 μ m, and should not exceed 0.25 μ m, in order to permit a smooth surface of the lower layer and hence a good base for an upper layer subsequently to be applied.

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In addition to the novel magnetic pigments, the lower layer may contain further components, such as polymeric binders, further pigments, antistatic agents, carbon blacks,

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lubricants, crosslinking agents, wetting agents, dispersants and the like, which are known per se and which are described in more detail in the abovementioned documents. For example, polyurethanes and vinyl polymers which, in a preferred embodiment, have polar groups, in particular sulfonate groups, are used as polymeric binders.

Known lubricants are, for example, fatty acids or fatty esters; for example, polyisocyanate is used as a crosslinking agent. In addition, the lower layer may contain, in addition to the magnetic pigment, further nonmagnetic pigments, for example $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 , TiO_2 , SiO_2 , Al_2O_3 , BaSO_4 , boron nitride, SnO_2 , CaCO_3 , ZrO_2 , TiC , SiC , Sb_2O_3 , ZnO , CeO_2 and carbon blacks, and further pigments.

The upper magnetic layer contains a ferromagnetic metal pigment or metal alloy pigment in high concentration. Examples of such metal pigments are likewise described in the abovementioned documents. The metal powder pigments contain, as main components, Fe, Ni and Co and, if required Al, Si, S, Sc, Ti, V, Cr, Cu, Y, Mo, Rh, Pd, Ag, Sn, Sb, Te, Ba, Ta, W, Re, Au, Hg, Pb, Bi, La, Ce, Pr, Nd, P, Mn, Zn, Sr or B, individually or as a mixture, and may have, on their surface, a protective coating to prevent oxidation or other harmful effects. The metal powders have a specific BET surface area of 40-80 m^2/g , the mean axial length is not more than 200 nm and the axial diameter is 10-30 nm. The coercive force is greater than 100 kA/m and the specific magnetization is greater than 80 Am^2/kg . Preferably, the upper magnetic layer has a coercive force of at least 140 kA/m and a residual induction of at least 250 kA/m. Furthermore, the upper magnetic layer contains the conventional additives, such as polymeric binders, which may also have polar groups, or corresponding binder mixtures and dispersants, nonmagnetic pigments, lubricants, curing agents, conductivity-enhancing compositions and wetting agents, all of which are known from the prior art.

The process for the preparation of the magnetic dispersion is known per se and comprises at least one kneading stage, one dispersing stage and, if required, one mixing stage, 5 which can be provided before and after the preceding stages. The respective stages may each be composed of two or more operations. In the preparation of the composition, all the starting materials, i.e. the ferromagnetic powder, the binders, the carbon blacks, the abrasives or supporting 10 pigments, the antistatic agents, the lubricants, the wetting agents and the dispersants and the solvents (for example tetrahydrofuran, methyl ethyl ketone, cyclohexanone or dioxane), may be added to the reactor unit right at the beginning of the process or later in the course of the 15 process. The crosslinking agent and, if required, a crosslinking catalyst are preferably added after the end of the preparation of the dispersion.

After fine filtration through narrow-mesh filters having a 20 mesh size of not more than 5 µm, the dispersions are applied by means of a conventional coating apparatus at speeds in the usual range, oriented in an essentially longitudinal recording direction in a magnetic field, dried and then subjected to a calender treatment and, if required, a 25 further surface-smoothing treatment.

"Essentially longitudinally oriented" means that the 30 magnetic particles are present oriented essentially in the recording direction in the plane of the layer but may also be arranged oriented obliquely with respect to the plane of the layer.

For the production of the novel magnetic recording media, 35 coating may be effected by means of bar coaters, knife coaters, doctor blade coaters, extruder coaters, reverse-roll coaters or combinations thereof. The two layers can be

applied simultaneously by the wet/wet or by the wet/dry method.

A knife coater which has at least one outlet orifice, preferably two or more outlet orifices, and is disclosed in German Laid-Open Application DOS 195 04 930 is particularly preferred for the production of the novel magnetic recording media. Also suitable is an extruder coater having at least one outlet orifice, preferably two or more outlet orifices, for the magnetic dispersions, the orifices being opposite the edge or the air gap of a magnet, on the other side of the flexible substrate, and the field lines of said magnet being essentially parallel to the running direction of the substrate. Such arrangements are disclosed in EP-B-0 654 165 or FR 2 734 500.

After the drying and calendering which follow the coating, the magnetic recording medium thus obtained is cut into the desired form for use and is subjected to the conventional electromagnetic and mechanical tests.

The measured value for the overwrite behavior is determined as follows in several steps.

1. Recording of a combined signal consisting of a short-wave component, preferably at 0.5 μm , and a long-wave signal with a wavelength of, for example, 3 μm . The long-wave component has a smaller amplitude than the short-wave signal, for example 20 dB lower. The combined signal is fed, prior to recording, into a limiter which delivers an output signal which has a constant amplitude and in which the long-wave signal is contained as a time-dependent modulation of the zero passes with a small deviation. This signal is recorded on the tape at the optimum working point.
2. Playback of the recording and measurement of the output level of the long-wave component to be overwritten.

3. Overwriting of the recording by the short-wave component.

4. Playback of the overwritten recording and further measurement of the output level of the long-wave component.

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The measured overwrite value OW is the difference in dB between the measured value of step 2 and that of step 4.

If such a measurement is carried out on a pair of magnetic tapes having a magnetic/nonmagnetic lower layer and roughly the same type of upper layer with the same layer thickness and the wavelength of the signal to be overwritten is varied, curves as shown, for example, in Fig. 3 are obtained for the measured overwrite value.

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The measured values show that the overwrite advantage of the novel magnetic recording material having a magnetic lower layer is effective over a wavelength range from about 10 μm to 0.6 μm . Particularly advantageous results are obtained when a very thin magnetic upper layer whose thickness is less than 0.3 μm is applied to a magnetic lower layer whose thickness is preferably 0.5-2 μm .

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Advantages are also evident when the thicknesses of the upper layers of the materials to be compared are not exactly the same. If, for example, a sample having a magnetic lower layer has a smaller thickness of the upper layer than the comparative sample having a nonmagnetic lower layer, the advantage resulting from the different layer thickness can be determined from magnetic flux measurements in conjunction with Figure 3, and the result can be corrected by this factor. In this case too, the overwrite behavior has advantages which are attributable to the presence of the magnetic lower layer in the novel magnetic recording medium.

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As shown in Figures 1 and 2, opposite trends as a function of the thickness of the upper layer are obtained in the

longer-wave range for the overwrite behavior and the output level. These opposite characteristics are shown once again in Figure 4; they apply both to tapes having a nonmagnetic lower layer and - at a higher level - to tapes having a magnetic lower layer.

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In the case of tape-like magnetic recording media having a nonmagnetic lower layer, it is difficult, if at all possible, to find a suitable compromise which offers both good overwrite behavior and an adequate output level. In contrast, the novel magnetic recording medium has the advantage that an additional reserve is obtained which can be used both for improving the overwrite behavior and for improving the output level, so that a compromise is possible

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and these properties can therefore be established in a specific manner.

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Figure 3 shows the advantages, achieved according to the invention, of the overwrite behavior for a magnetic lower layer in comparison with a nonmagnetic lower layer.

The Examples which follow illustrate the invention without restricting it.

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Example 1:

Composition of the upper layer	Parts by weight
- Ferromagnetic metal pigment	100
H _c : 183 kA/m; σ _s : 140 Am ² kg ⁻¹	
BET: 54 m ² /g; l: 100 nm; d: 20 nm	
Fe:Co=76% by weight:24% by weight	
- α-Alumina	
Particle diameter: about 220 nm	10
- Carbon black	
BET: 35 m ² /g; primary particle size: 50 nm	1.5
- VC copolymer having polar groups	8
Degree of polymerization: 300	

VC content: 85% by weight; epoxide
content: 3% by weight

Content of SO₃Na: 65 mmol/kg

- Polyurethane having polar groups 6

5 Mw=30,000; Tg (DSC): 70°C

Content of SO₃Na: 100 mmol/kg

- Stearic acid/palmitic acid 1:1 2.5

- Butyl stearate 0.5

- Crosslinking agent 2.2

10 Reaction product of

3 mol of toluylene diisocyanate with

1 mol of trimethylolpropane

- Solvents (THF/dioxane 1:1) 530

15 2. Composition of the lower layer Parts by weight

Chromium oxide (73 m²/g BET;

H_c: 21 kA/m) 100

Carbon black (primary particle
size: 25 nm) 29

20 Vinyl polymer having polar groups *) 13

Polyurethane having polar groups *) 15

Stearic acid/palmitic acid 1.5

Butyl stearate 1

Crosslinking agent 3

25 Solvents (THF, dioxane) 658

For characteristic data, cf. composition of the upper
layer.

30 The dispersions ready for coating the upper and lower layers
were prepared by kneading in a batch kneader, dilution in
portions, subsequent milling in a stirred ball mill and
making up with the addition of the crosslinking agent, of
butyl stearate and of the amounts of solvent required for
establishing the coating viscosities.

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The application of both layers to a PET film (thickness:
6.4 µm) provided beforehand with a 0.5-0.6 µm thick backing

coating was effected by the wet-in-wet method by means of a coating apparatus as described in more detail in German Laid-Open Application DOS 195 04 930. Before drying, the coated film was passed through an orientation zone, consisting of a plurality of coils having a field strength of 200 kA/m, for orientation of the magnetic pigments. After drying at 80°C, the film web was surface-treated in a steel/steel calender having 6 gaps at 85°C and a nip pressure of 200 kg/cm and then slit into 8 mm wide video tapes. The layer thicknesses for the upper and lower layer were 0.26 µm and 1.1 µm, respectively.

Example 2:

The procedure was as in Example 1, except that the upper layer had a thickness of 0.12 µm.

Example 3:

The procedure was as in Example 1, except that the lower layer had the following composition:

	Composition of the lower layer	Parts by weight
25	α -Fe ₂ O ₃ (54 m ² /g BET)	50
	Co-doped γ -Fe ₂ O ₃ (36 m ² /g BET; H _c 66 kA/m)	50
	Carbon black (primary particle size: 25 nm)	29
	Vinyl polymer having polar groups	13
	Polyurethane having polar groups	15
30	Stearic acid/palmitic acid	1.5
	Butyl stearate	1
	Crosslinking agent	3
	Solvents (THF, dioxane)	580

The thickness of the upper layer was 0.125 µm and that of the lower layer 1.1 µm.

Comparative Example 1:

The procedure was as in Example 1, except that the lower layer had the following composition:

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	Composition of the lower layer	Parts by weight
	Vinyl polymer having polar groups	8
10	Polyurethane having polar groups	4
	Chromium oxide ($70 \text{ m}^2/\text{g}$ BET, $H_c: < 0.5 \text{ kA/m}$)	63
	Al_2O_3 (primary particle size $0.4 \mu\text{m}$)	12
	Carbon black (primary particle size 30 nm)	25
15	Lubricant	10.6
	Dispersant	2
	Crosslinking agent	4
	Solvents (tetrahydrofuran, dioxane)	4/6

20 The thickness of the upper layer was $0.15 \mu\text{m}$ and that of the lower layer $1.4 \mu\text{m}$.

25 Since the absolute layer thicknesses of the upper and lower layers are not measurable directly with the necessary accuracy, they were determined computationally by measuring the magnetic flux values using a commercial vibrating-sample magnetometer (for example a vibrating-sample magnetometer from Digital Measurement Systems) with the aid of calibration samples (thin SEM sections).

30

Comparative Example 2:

The procedure was as in Example 1, except that the lower layer had the following composition:

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	Composition of the lower layer	Parts by weight
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$\alpha\text{-Fe}_2\text{O}_3$ (54 m ² /g BET)	50
Metal pigment (57 m ² /g BET; H _c : 134 kA/m)	50
Carbon black (primary particle size: 25 nm)	29
Vinyl polymer having polar groups	13
5 Polyurethane having polar groups	15
Stearic acid/palmitic acid	1.5
Butyl stearate	1
Crosslinking agent	3
Solvents (THF, dioxane)	670

10 The layer thicknesses of the upper and lower layers were:
0.19 μm and 1.5 μm.

Comparative Example 3:

15 A monolayer tape having a layer thickness of 1.1 μm was produced, only the upper layer having the composition described in Example 1 being cast.

20 Table 1 below shows the results of the measurements from the Examples described above.

25 Since the overwrite behavior measured at a wavelength of 3 μm is representative of the overwrite advantage, the values obtained here are stated as being representative of the entire curve.

The individual measured values have the following meanings:

30	Thickness UL	= Thickness of the upper layer, dry
	H _c UL	= Coercive force of the upper layer
	MrUL	= Residual induction of the upper layer
	H _c LL	= Coercive force of the lower layer
	MrLL	= Residual induction of the lower layer
35	Output level 3 μm	= Original playback level at 3 μm wavelength
	OW 3 μm	= Original playback level minus playback level after overwriting = overwrite damping

Overwritten signal: 3 μm wavelength

Overwriting signal: 0.5 μm wavelength

ΔOW 3 μm

= Difference between the overwrite damping
of the example tape and the overwrite
damping of a comparative tape having a
nonmagnetic lower layer

Output level

0.5 μm

= Playback level of the overwriting signal
(data signal)

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Table 1

Patent claims

1. A magnetic recording medium comprising at least two layers on a nonmagnetic substrate, the lower layer containing at least one binder and one pigment and the upper binder-containing layer containing a metal powder or metal alloy powder as magnetic pigment and having a thickness of less than $0.3 \mu\text{m}$, wherein the lower layer contains a magnetic pigment, the coercive force H_c of the lower layer being not more than two thirds of the coercive force H_c of the upper layer and the residual induction Mr of the lower layer being at least 32 kA/m .
2. A magnetic recording medium as claimed in claim 1, wherein the coercive force H_c of the lower layer is not more than half the coercive force of the upper layer.
3. A magnetic recording medium as claimed in claim 1, wherein the residual induction Mr of the lower layer is from 32 to 150 kA/m .
4. A magnetic recording medium as claimed in any of claims 1 to 3, wherein the layer thickness of the lower layer is from 0.5 to $2 \mu\text{m}$.
5. A magnetic recording medium as claimed in any of claims 1 to 4, wherein the magnetic pigment in the lower layer is an acicular magnetic chromium oxide pigment having a coercive force H_c of from 15 to 40 kA/m and a BET surface area of from 50 to $100 \text{ m}^2/\text{g}$.
6. A magnetic recording medium as claimed in claim 5, wherein the coercive force of the magnetic chromium oxide pigment in the lower layer is from 20 to 30 kA/m .

7. A magnetic recording medium as claimed in any of claims 1 to 4, wherein the magnetic pigment in the lower layer is a doped or undoped $\gamma\text{-Fe}_2\text{O}_3$ pigment having a coercive force H_c of from 15 to 80 kA/m and a BET surface area of from 30 to 50 m^2/g .
5
8. A magnetic recording medium as claimed in claim 7, wherein the magnetic pigment in the lower layer is a cobalt-doped $\gamma\text{-Fe}_2\text{O}_3$ pigment.
10
9. A magnetic recording medium as claimed in claim 7 or 8, wherein the coercive force of the $\gamma\text{-Fe}_2\text{O}_3$ pigment in the lower layer is from 50 to 70 kA/m.
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10. A magnetic recording medium as claimed in any of claims 1 to 9, wherein the magnetic pigment in the lower layer has a mean particle length of from 0.05 to 0.25 μm .
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11. A magnetic recording medium as claimed in claim 10, wherein the mean particle length of the magnetic pigment in the lower layer is from 0.1 to 0.2 μm .
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12. A magnetic recording medium as claimed in claim 1, wherein the lower layer additionally contains a non-magnetic pigment.
13. A magnetic recording medium as claimed in claim 12, wherein the nonmagnetic pigment is $\alpha\text{-Fe}_2\text{O}_3$.

Abstract

Magnetic recording medium having a high recording density

5 Digital recording methods in which the recording medium does not pass an erasing field prior to a recording have recently become known. Such recording media must consequently have good overwrite behavior. It was found that this requirement is met by recording media composed of two layers, the upper
10 layer containing a metal powder or metal alloy powder and having a thickness of less than 0.3 μm and the lower layer containing a magnetic pigment. The coercive force of the lower layer is not more than two thirds of the coercive force of the upper layer and the residual induction of the lower
15 layer is at least 32 kA/m.

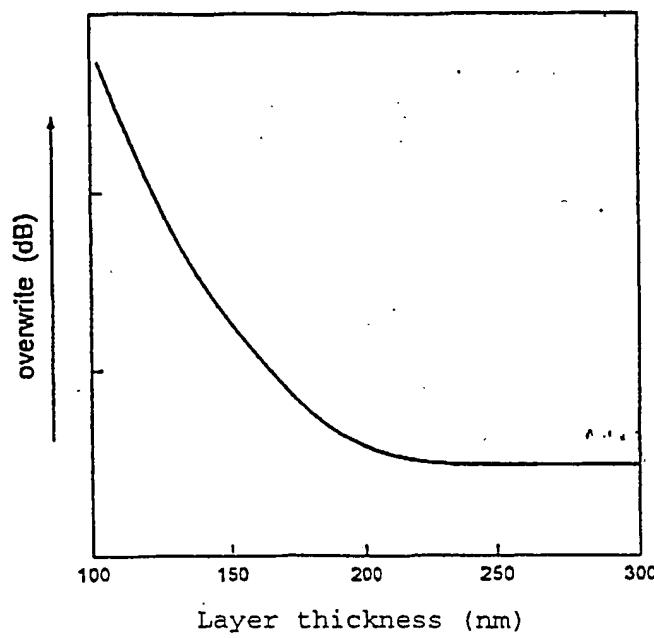


Fig. 1

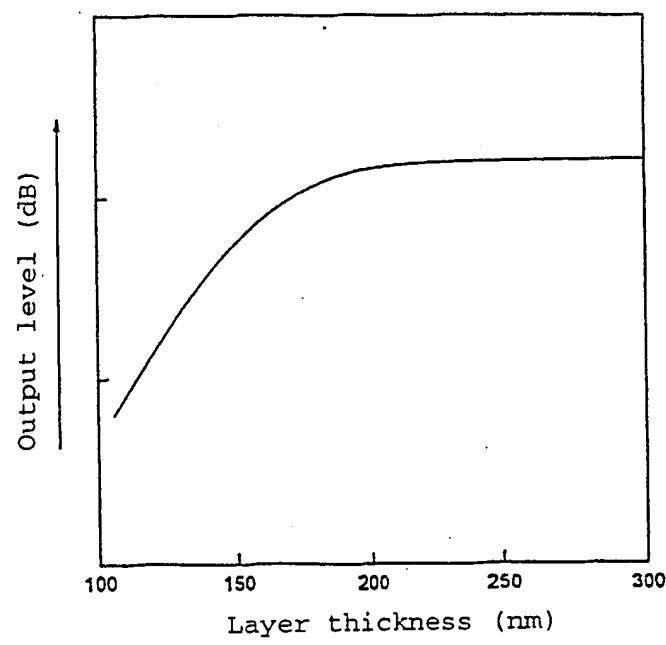


Fig. 2

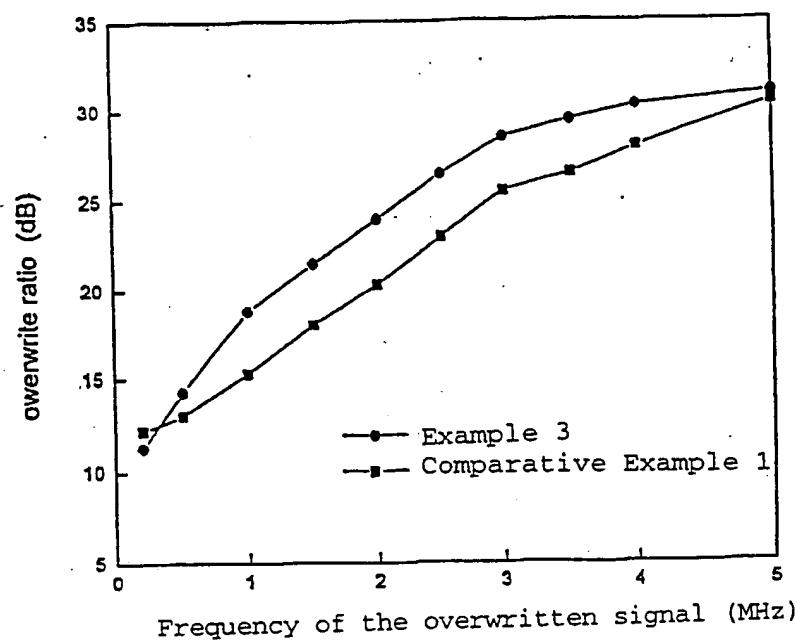


Fig. 3

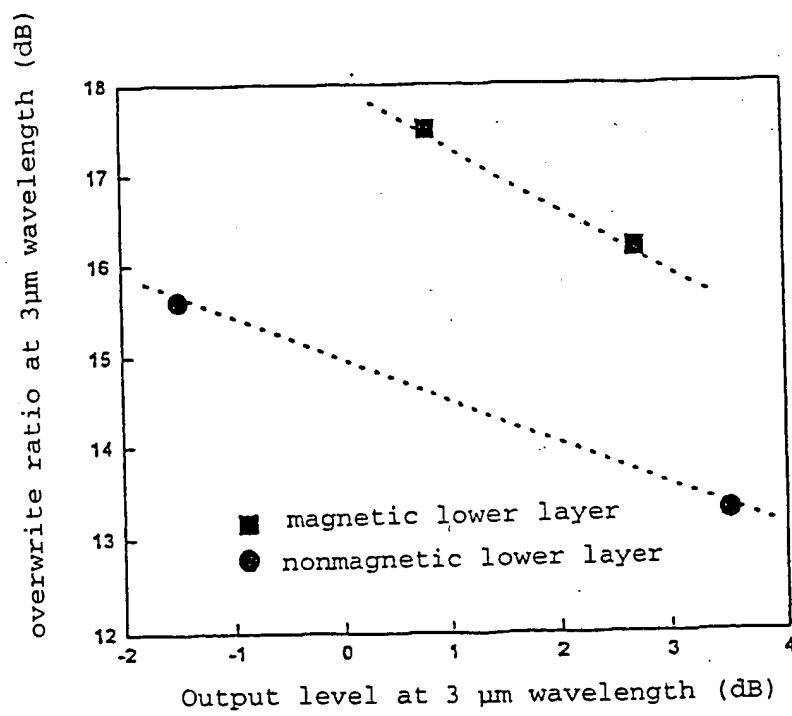


Fig. 4